Absorbance and induced fluorescence of rain water in a temperate coastal embayment (Ría de Vigo, NW Spain)

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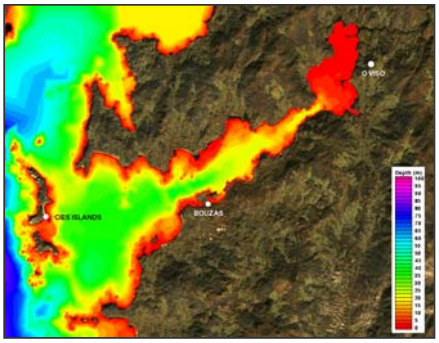
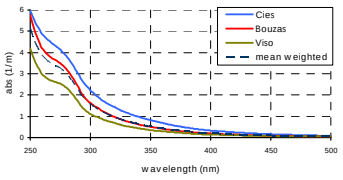
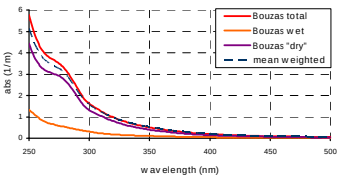
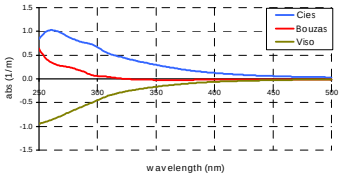
The dynamics of the Ría de Vigo, a large embayment in the NW Iberian coast, is primarily controlled by remote winds and secondarily by continental runoff. It is characterised by a 2-layered residual circulation pattern, positive under upwelling-favourable northerly winds and negative under downwelling-favourable southerly winds. The spring and autumn phytoplankton blooms occur during the seasonal transitions from downwelling to upwelling conditions and vice versa, respectively. Copious rainfall during those transitional periods could be a significant source of organic and inorganic nutrients to the surface layer of the ría.



The chemical composition of rain water (total deposition) in contrasting rural, urban and marine environments of the Ría de Vigo was monitored on a daily basis during 2 years. Dissolved organic carbon (DOC), absorbance, and induced fluorescence spectra are used to quantify and characterise the organic loads of rain water.

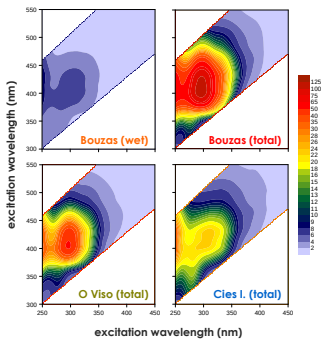


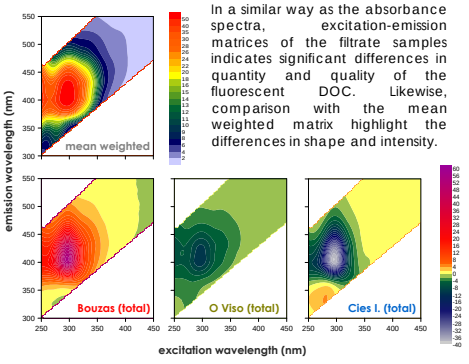




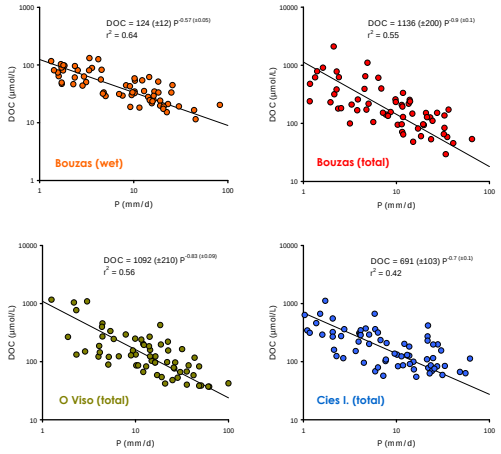
Absorbance spectra of the filtrated samples show different quantity and quality of the coloured DOC at each station. This fact is more obvious when comparing each sample with the mean weighted.

The wet fraction only represents a small fraction of the total absorbance.

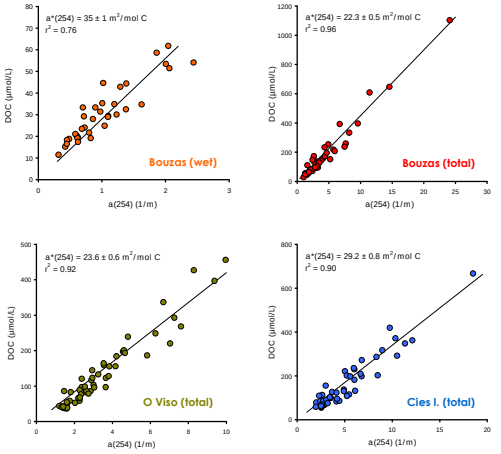




In a similar way as the absorbance spectra, excitation-emission matrices of the filtrate samples indicates significant differences in quantity and quality of the fluorescent DOC. Likewise, comparison with the mean weighted matrix highlight the differences in shape and intensity.



The concentration of dissolved organic carbon (DOC) correlated inversely ($r^2 > 0.42$; $p < 0.001$) with the daily precipitation rate (P) following the equation $DOC = a \cdot P^b$, where a is the DOC concentration at P = 1 mm/d and b is the dilution factor. The coefficient a was around 1050 ± 200 µmol/L in the rural and urban stations but it was significantly lower ($p < 0.05$), 650 ± 100 µmol/L, in the marine station. The coefficient b was -0.8 ± 0.1 at the three sites.



Linear regressions through the origin ($r^2 > 0.90$, $p < 0.001$) were obtained between DOC and the absorption coefficient at 254 nm, a(254), but with different slopes: the absorptivity at 254 nm, a*(254), was significantly higher ($p < 0.005$) at the marine station (29.2 ± 0.8 m²/mol C) than at the rural (23.6 ± 0.6 m²/mol C) and urban (22.3 ± 0.5 m²/mol C) sites.

station name	station type	n		a(254) / a(365)		FDOMI/FDOMa		Φ (340)	
Bouzas (wet)	urban	68	average	13.5	a	11.8	a	1.4	a
			S.D	4.6		17.2		0.5	
Bouzas (total)	urban	64	average	13.2	a	6.4	b	2.7	b
			S.D	2.7		12.0		0.6	
O Viso (total)	rural	65	average	13.5	a	7.6	b	2.7	b
			S.D	3.7		10.4		0.8	
Cies Islands (total)	marine	67	average	9.0	b	11.3	a	1.6	c
			S.D	1.5		12.8		0.4	

Rain water at the marine station also presented significantly lower ($p < 0.001$) values of the a(254)/a(365) ratio, 9.0 compared to >13.2, and the fluorescence quantum yield at 340 nm, Φ(340), 1.6% compared to 2.7%. Conversely, the ratio of the induced fluorescence at peak-T (Ex/Em = 280nm/350nm) and peak-A (Ex/Em = 250/450), characteristic of protein- versus humic-like fluorophores, was significantly higher ($p < 0.001$) at the marine (11.3) than at the urban and rural sites (<7.6).

Concomitant collection of wet deposition samples at the urban site yielded that a = 95 ± 10 µmol/L, b = -0.57 ± 0.05, a*(254) = 30.6 ± 0.9 m²/mol C, a(254)/a(365) = 13.5, Φ(340) = 1.4%, and peak-T/peak-A = 11.8.

CONCLUSIONS:

These optical indices suggest that: (i) 100% of the DOC in rainwater is coloured; (ii) the aromaticity of rain water in the marine site is significantly higher than in the urban and rural sites; and (iii) aromatic amino acids are proportionally more abundant than aromatic humic substances in the marine site.

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